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A DISSERTATION

Submitted to the Faculty of the Graduate College of the State University of Iowa in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

BY

ARTHUR ROY FORTSCH

IOWA CITY, IOWA
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THE FREE ENERGY OF DILUTION AND THE ACTIVITIES OF THE IONS OF HYDROGEN IODIDE IN AQUEOUS SOLUTIONS.

Because of their anomalous behavior solutions of strong electrolytes have long occupied the attention of numerous investigators. Many attempts have been made to provide a theoretical explanation of the abnormalities. Of the various solution properties the free energies of dilution and the activities of the ions have been especially studied. From calculations based on the assumption that a common ion at any given concentration has the same mobility regardless of the associated ion G. N. Lewis[1] concluded that the chlorides, bromides, and iodides of hydrogen and of the alkali halides are equally dissociated in tenth molal solutions. In order to explain changes in transport numbers he advances two hypotheses: (1) "that all the ions increase in mobility with increasing ion-concentration, the increase being relatively greater, the greater the original mobility; (2) that all the ions decrease in mobility with increasing ion-concentration, the decrease being greater the smaller the original mobility." He favors the first of these and advances as probable causes: (1) a gradual dehydration which although undoubtedly present, does not play a dominant part, and (2) an added increase in the ordinary conductivity of the electrolyte due to a conduction of the Grotthus type.

MacInnes[2] using the same assumption has found that the alkali chlorides are equally dissociated in hundredth molal solutions. His observations led him to assume that the activity of the chloride ion is independent of the cation associated with it. The similarity of the potassium ion and the chloride ion with respect to atomic weight, atomic volume, ionic mobility, and other properties, led him to assume that their activities are also equal in solutions of potassium chloride.

Of the various investigations only those most closely connected

[1] J. Am. Chem. Soc., 34, 1631 (1912).
[2] J. Am. Chem. Soc., 41, 1086 (1919).

with this research will be mentioned here. Noyes and MacInnes[3] have computed the mean activity coefficients of the ions of potassium chloride, hydrogen chloride, lithium chloride, and potassium hydroxide. Harned[4,5] on the basis of theoretical considerations has developed a semi-empirical relation between the activity coefficient of an electrolyte and the molal concentration and has calculated the activities of the various ions from the experimental data of himself and others. He concludes that the assumptions of Noyes and MacInnes[6] are true within certain limits and that the theory of complete ionization of strong electrolytes is a good working hypothesis. His work gives us a very valuable summary of preceding investigations. In connection with this theory of complete dissociation of strong electrolytes, we may note that it was first suggested by Noyes[7] and was further developed and substantiated by Milner[8], Ghosh[9], Bjerrum[10], Bronsted[11], Hill[12], and others. Finally we have the very complete work of Lewis and Randall[13]. They discuss the four methods of experimentally determining activity coefficients, namely: activity from vapor pressure of the solvent; activity from vapor pressure of the solute; activities from electromotive force; and activity coefficients from freezing point data. They also give the numerical values of the activities of the various ions at different concentrations, determined by one or more of the above methods.

A very important relation in regard to ionic activity was pointed out by Lewis and Randall[14] and at about the same time by Pearce and Hart[15]. Lewis and Randall, using the experimental data of Bates and Kirschmann[16] on partial vapor pressures of the hydrogen halides, showed that the activities of the

[3] J. Am. Chem. Soc., 42, 239 (1920).
[4] J. Am. Chem. Soc., 42, 1808 (1920).
[5] J. Am. Chem. Soc., 44, 252 (1922).
[6] loc. cit.
[7] Congress. Arts & Sciences, St. Louis Exposition, 4, 389 (1904).
[8] Phil. Mag., (6) 23, 551 (1912); 25, 753 (1913); 35, 352 (1918).
[9] J. Am. Chem. Soc., 113, 449 (1918); 113, 627 (1918); 113, 707 (1918).
[10] Z. Electro Chem., 24, 321 (1918); Z. Anorg. Chem., 109, 275 (1920).
[11] J. Am. Chem. Soc., 42, 761 (1920).
[12] Ibid., 43, 254 (1920).
[13] J. Am. Chem. Soc., 43, 1152 (1921).
[14] loc. cit.
[15] J. Am. Chem. Soc., 43, 2483 (1921).
[16] J. Am. Chem. Soc., 41, 1991 (1919).

chloride, bromide, and iodide ions are equal at equal concentrations. Pearce and Hart, using the electromotive force method, showed that the chloride and bromide ion activities are equal at equal concentrations. It was considered expedient in view of these facts to add to the investigations by making a study of the free energy of dilution and the activities of the ions in aqueous solutions of hydrogen iodide.

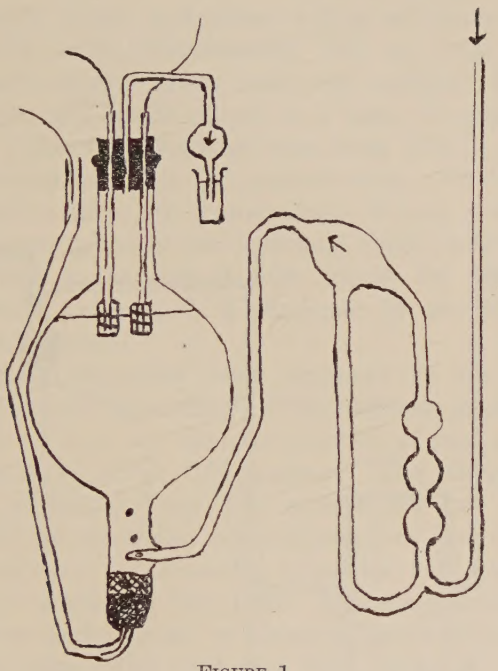

FIGURE 1

Apparatus and Materials.

The method used in this research is similar to that of Linhart[17], the iodide being substituted for the chloride. The silver iodide was made by precipitation from a solution of potassium iodide by means of silver nitrate solution. The potassium iodide was purified by crystallizing twice from conductivity water. The silver nitrate was the "Baker's Analysed" product. The precip-

[17] J. Am. Chem. Soc., 41, 1175 (1919).

itate was washed first with distilled water until the washings gave no test for iodides, and then washed several times with conductivity water. The whole operation was carried out at night. It was finally stored under conductivity water, care being

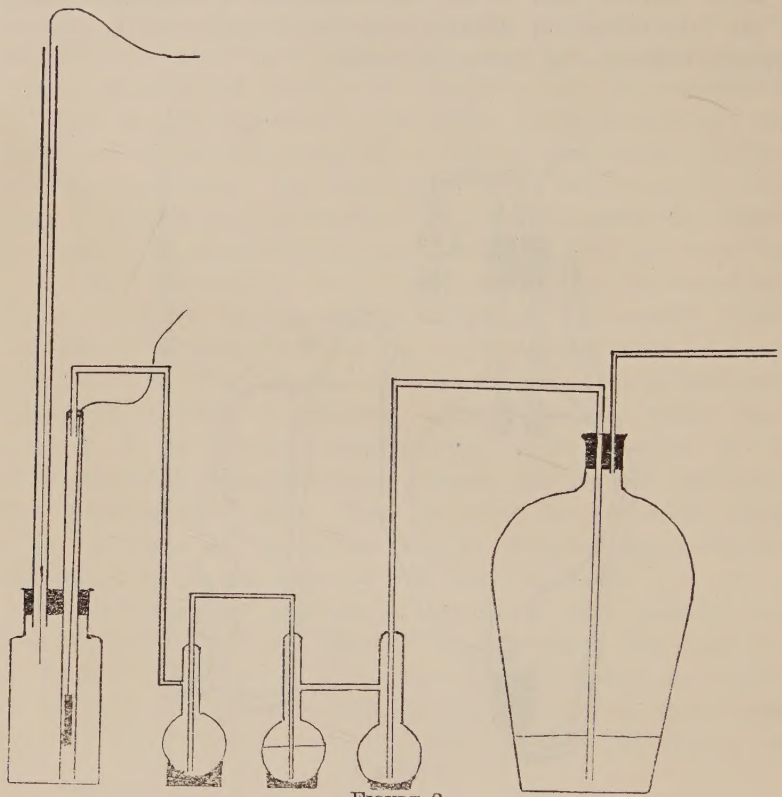

FIGURE 2

used to exclude all light from the product. By using these precautions the silver iodide could be preserved indefinitely with no apparent darkening.

The metallic silver was obtained by electrolysis of silver nitrate solution, using a platinum wire anode and a current of 4 to 5 amperes. This gave a finely divided crystalline mass of metallic silver. The silver after being carefully washed was stored under conductivity water until needed.

The hydrogen iodide was made by passing hydrogen sulphide gas into an aqueous suspension of resublimed iodine. The product was distilled and the fraction of constant boiling point separated. This was kept in a flask over a trace of red phosphorus and was freshly distilled in a current of hydrogen gas when needed.

In making up the solutions, approximately the required amount of hydrogen iodide was added to conductivity water which had been previously boiled, and about a liter of solution made up. The cell which held approximately 550 c.c. was thoroughly cleaned, rinsed several times with the solution, filled to the proper volume, and finally placed in a large oil-bath to come to equilibrium. The time required was from four to eight days, depending somewhat upon the concentration. The bath heater was controlled to give any temperature desired within $\pm 0.03°$. The exact concentration of the hydrogen iodide used in each cell was determined at the end of each set-up, the iodine content being accurately determined in duplicate by precipitation with silver nitrate solution.

The hydrogen electrodes were prepared by the method of Lewis, Brighton, and Sebastian[18]. Two platinum gauze electrodes were electrolysed in a one per cent solution of platinum chloride with a current of about 0.05 ampere. The direction of the current was alternated every five minutes for two hours. The preparation of the electrodes was completed by electrolysing first in a dilute solution of potassium hydroxide and then in dilute sulphuric acid solution. They were thoroughly washed in conductivity water and allowed to stand in conductivity water for several hours, after which time they were placed in the cell.

The hydrogen was obtained by electrolysis of sodium hydroxide solution. The gas was passed through a solution of potassium pyrogallate, then through concentrated sulphuric acid, and on through the saturator into the cell. The saturator was merely a series of bulbs through which the hydrogen passed before entering the cell. This saturator contained a solution of the same strength as that in the cell and thus any change in concentration due to unsaturated hydrogen gas was avoided. The flow of the

[18] J. Am. Chem. Soc., 39, 2245 (1917).

hydrogen through the cell was regulated by means of a stop cock to about sixty bubbles per minute. The cell and saturator are shown in Fig. 1, while Fig. 2 shows the generator and the storage bottle through which the hydrogen passed before entering the cell.

The measurement of the potentials was made on a Wolff potentiometer, the reference standard being a certified cadmium-Weston cell. (No. 4554; 1.01871 volts at 23°).

Accuracy of Method.

Electromotive force readings were taken on the two electrodes independently and unless the variation between the two was less than 0.04 m. v. the process of preparation was repeated. Cases where a repetition was necessary were very rare. All electromotive force readings were corrected by applying the formula:

$$E = \frac{.00019837\ T}{2} \log_{10} \frac{760}{x}$$

where E is the correction, T the absolute temperature, and x is the pressure of the hydrogen. The value of x was determined by a standard barometer the readings being corrected for latitude, altitude, and temperature.

Preliminary experiments were made to determine the effect of the rate of bubbling. It was found that the rate could be varied from 30 to 250 per minute without affecting the constancy of the readings.

The temperatures of the experiment were 25°, 30°, and 35°. They were taken in the order named and then to ascertain whether any changes had occurred during the experiment the temperature was lowered to 25° and readings were again taken. The time required to complete this series was ten days. In the preliminary work it was found that there is a variation which becomes apparent when the electrodes are left in the solution over sixty hours. But by removing the electrodes, allowing them to stand in concentrated nitric acid for an hour or more, and replatinizing this effect was reduced to 0.10 m. v. or less in solutions whose concentration was below 0.02 M. per 1000 grams of water. In the more concentrated solutions, however, it was

apparently impossible to eliminate the variation, but at any one temperature the electromotive forces became constant showing that equilibrium had been reached. When four consecutive readings taken two hours apart which differed among themselves by less than 0.04 m. v. were secured, this was considered as evidence that equilibrium had been attained. The greatest variation of the electromotive force readings between the initial 25° set and the final 25° set was recorded at the highest concentration. In this case it was 0.85 m.v. Furthermore, at concentration 0.12972 M a slight turbidity was obtained by adding a chloride to the solution secured by allowing the electrodes to stand in concentrated nitric acid, but there was not a weighable amount of silver chloride. At concentration of 0.24608 M. the amount of silver was larger but did not exceed a few milligrams. At higher concentrations than this the amount of silver deposited on the platinum electrodes became considerable and no consistent readings could be obtained.

Measurement of the Cells.

Table I gives the final values of the electromotive force of the cells at various concentrations and at 25°, 30°, and 35°.

TABLE I.

Electromotive Force of the Cells:

H_2 | HI (c) ..... HI (c), AgI | Ag.

c. 1000 g.	E_{25}. volts.	E_{30}. volts.	E_{35}. volts.
0.24608	—0.06905	—0.06864	—0.06829
0.12972	—0.03615	—0.03556	—0.03531
(0.10000)	—(0.02273)	—(0.02202)	—(0.02162)
0.07914	—0.01210	—0.01128	—0.01073
0.05049	+0.01006	+0.01128	+0.01235
0.01981	+0.05735	+0.05931	+0.06083
0.01045	+0.08825	+0.09060	+0.09262
0.00505	+0.12417	+0.12707	+0.12964
(0.00500)	+(0.12453)	+(0.12744)	+(0.13001)

The values of E (in parenthesis) for the concentration 0.005 were obtained by assuming E as an empirical quadratic function

of (c) using the three concentrations, 0.01981, 0.01045, and 0.00505. Those for 0.100 were obtained in a similar manner using concentrations, 0.24608, 0.12972, and 0.07914. It will be noted that a change of sign occurs between the concentrations 0.07914 and 0.05049. This is due to the fact that silver iodide is extremely insoluble; a small concentration of hydrogen iodide is sufficient by the common ion effect to reduce the concentration of the silver ion to such an extent that the potential of Ag | AgI, HI is less than the potential H_2 | HI. So far as the author has been able to ascertain this circumstance is unique in investigations of free energies and activities of ions.

Free Energy Change Attending the Cell Reaction.

Table II gives the free energy change accompanying the cell reaction. The free energy decrease (—ΔF) in joules is obtained by multiplying the corresponding value of the electromotive force in volts by 96494. The data are self-explanatory.

TABLE II.

Free Energy Change Attending the Cell Reaction.

c.	$(-\Delta F)_{25}$.	$(-\Delta F)_{30}$.	$(-\Delta F)_{35}$.
1000 g.	joules.	joules.	joules.
0.24608	—6662.9	—6623.3	—6589.6
0.12972	—3488.3	—3431.3	—3407.2
(0.10000)	—(2193.3)	—(2124.8)	—(2086.2)
0.07914	—1167.6	—1088.5	—1035.4
0.05049	+970.3	+1088.5	+1191.7
0.01981	+5533.9	+5723.1	+5869.7
0.01045	+8515.6	+8742.4	+8937.3
0.00505	+11981.7	+12261.5	+12509.5
(0.00500)	+(12016.4)	+(12297.2)	+(12545.2)

Temperature Coefficients of Free Energy Decrease, and Heat-Content Decrease Accompanying the Cell Reaction.

In Table III are given the values of α and β for the various concentrations, calculated from the relation:

$$(-\Delta F)_t = (-\Delta F)_{25} (1+\alpha (t-25)+ \beta (t-25)^2).$$

The values of the decrease in heat-content $(-\Delta H)_{25}$ are given in column four of the table, being computed from the formula:

$$(-\Delta H)_{25} = (-\Delta F)_{25} \quad (1-298.09\alpha).$$

Upon substituting the expression for $(-\Delta F)$ as a temperature function for any given concentration in the fundamental thermodynamic equation:

$$\frac{d}{dT}\left(\frac{(-\Delta F)}{T}\right) = \frac{+\Delta H}{T^2},$$

performing the differentiation indicated, and rearranging the terms the above relation for $(-\Delta H)_{25}$ is obtained

TABLE III.

Values of Temperature Coefficients and Heat-Content Decrease at the Various Concentrations.

c.	α	β	$(-\Delta H)_{25}$.
1000 g.	X 10^6	X 10^7	joules.
0.24608	—1277.1	+177.1	—9199.5
0.12972	—4211.3	+1886.3	—7867.2
(0.10000)	—(7609.5)	+(2726.5)	—(7168.1)
0.07914	—16151.6	+4453.6	—6789.1
0.05049	+25909.5	—3091.8	—6523.8
0.01981	+7607.7	—1539.6	—7015.9
0.01045	+5699.7	—747.8	—5952.6
0.00505	+4950.4	—530.9	—5699.2
(0.00500)	+(4950.1)	—(549.4)	—(5715.0)

It will be noted that the values α and β change sign between the concentrations 0.05049 M. and 0.07914 M. Ellis[19] likewise notes a change of sign of α for hydrochloric acid between the concentrations 0.33757 M. and 0.10040 M. In his case, however, the change is due to a distinct change in the temperature effect, whereas, in the case of hydriodic acid in every instance the free energy of the cell reaction is greater the higher the temperature, the change being caused by a change in the sign of the electromotive force of the cell. At some concentration intermediate to 0.05049 M. and 0.07914 M. the electromotive force and hence the free energy decrease is zero. Thus the values of α must

[19] J. Am. Chem. Soc., 38, 737 (1916).

change from a small negative number to an infinitely large negative number on the one hand, and from an infinitely large positive number to a small positive number on the other hand. Except for the one value—7015.9 at concentration 0.01981 M. the values of $-\Delta H$ show an increase with decreasing concentration similar to those found by Ellis[20] for hydrochloric acid. The values for hydriodic acid are, however, much smaller and are negative instead of positive.

Free Energy Decrease Accompanying the Transfer of One Mole of Hydrogen Iodide From the Various Concentrations (c) to 0.100 M.

From the free energy decrease attending the cell reaction at the various concentrations we can obtain, by taking the algebraic sum, the free energy decrease attending the transfer of one mole of hydrogen iodide from a solution of any given concentration to one exactly 0.100 M. These values are given in Table IV.

TABLE IV.

Free Energy Decrease Attending the Transfer of One Mole of Hydrogen Iodide from Concentration (c) to 0.100 M.

c.	$(-\Delta F)_{25°}$.	$(-\Delta F)_{30°}$.	$(-\Delta F)_{35°}$.
1000 g.	joules.	joules.	joules.
0.24608	+4469.6	+4498.5	+4503.4
0.12972	+1295.0	+1306.5	+1321.0
0.07914	—1025.7	—1036.3	—1086.2
0.05049	—3163.6	—3213.3	—3277.9
0.01981	—7727.2	—7847.9	—7955.9
0.01045	—10708.9	—10867.2	—11023.5
0.00505	—14175.0	—14386.3	—14595.7
(0.00500)	—(14209.7)	—(14422.0)	—(14631.4)

For the sake of comparison let us consider the transfer of one mole from 0.01045 M. to 0.100 M., and from 0.00500 M. to 0.05049 M. In the first case the value of $-\Delta F_{25}$ is 10709. joules, in the second case $-\Delta F_{25}$ is 11146 joules. For hydrochloric acid Noyes and Ellis[21] found for the transfer from 0.00948 to

[20] loc. cit.

[21] J. Am. Chem. Soc., 39, 2532 (1917).

0.100 M.—ΔF_{25} to be 11044. joules, and from 0.003378 M. to 0.03324 M., 10924 joules. As these changes are approximately tenfold they may be compared with the theoretical value 11418. joules. ($-\Delta F = 2.303\ N\ R\ T$). It will be seen that during the range of concentration 0.00500 to 0.05049 M., hydrogen iodide functions more nearly as a perfect solute than hydrogen chloride. As we shall see later, this is also shown by the values of the activity coefficients.

The Calculation of Activity Coefficients.

The values of the electromotive force at concentration 0.00500 M. were found by assuming that E is a quadratic function of (c) using the values 0.00505, 0.01045, and 0.01981 for the concentrations and the corresponding values of the electromotive forces at 25°C. The cell combination was of the type: $H_2|HI(c=.005...HI(c=.005)$, $AgI\,|\,AgAg\,|\,AgI, HI(c)....HI(c)|H_2$. The product of the activity coefficients of the ions has been computed according to the usual formula:

$$-\Delta F = EF = RT \log \frac{a_1 + . a_1 -}{a_2 + . a_2 -} = RT \log \frac{(c_1)^2 \alpha_1 + . \alpha_1 -}{(c_2)^2 \alpha_2 + . \alpha_2 -}$$

where a_1, a_2, ...refer to activity coefficient products, and α_1, α_2, ...refer to activity coefficients, the other symbols having their usual significance. These computations have been made on the assumption that for 0.005 M. hydrogen iodide $\alpha + . \alpha -$ has the same value as for 0.005 M. hydrogen chloride. According to Noyes and MacInnes[22] this value is $(965)^2$ or .9312, while according to Lewis and Randall[3] it is $(.947)^2$ or .8968. Column three of Table V gives the values of $\alpha_{H}^{+} . \alpha_{I}^{-}$ using .9312 as a basis, while column four gives the activity coefficient products using .8968 as a basis. These values were plotted against the concentrations on large scale and the values of $\alpha_{H}^{+} . \alpha_{I}^{-}$ corresponding to round concentrations were read off. The square roots of these values give us the activity coefficients. These are given in Table VI while similar values

[22] loc. cit.
[23] loc. cit.

for hydrochloric acid are given in adjoining columns for comparison.

TABLE V.

Activity Coefficient Products.

c	Δ E.	$\alpha_+.\alpha_-$ H I	$\alpha_+.\alpha_-$ H I
1000 g.	volts.		
0.00500	0.00000	.9312	.8968
0.01045	0.03628	.8748	.8331
0.01981	0.06718	.8111	.7724
0.05049	0.11447	.7866	.7491
0.07914	0.13663	.7585	.7223
0.12972	0.16068	.7200	.6856
0.24608	0.19358	.7201	.6857

TABLE VI.

Activity Coefficients $\sqrt{\alpha_+.\alpha_-}$ at Round Concentrations.

c.	HI.	HCI.	HI.	HCI.
1000 g.	(exp.)	(N-M)	(exp.)	(L-R)
0.005	.965	.965	.947	.947
0.010	.937	.932	.920	.924
0.020	.901	(.899)	.886	.894
0.030	.893	.880	.877	——
0.050	.884	.855	.868	.860
0.100	.862	.823	.846	.814
0.200	.849	.796	.834	.783

On the assumption that the activity of the ions is independent, and that the activities of the chloride, bromide, and iodide ions are equal, we should expect the same activity coefficients for hydrogen iodide as were found for hydrogen chloride. Whether we use the value .965 or .947 for the activity coefficient of 0.005 M. hydrogen iodide, a glance at Table VI shows that the coefficients are not equal throughout the whole range of concentrations investigated. The agreement with similar magnitudes for hydrochloric acid by Noyes and MacInnes[24] is good where the concentrations are less than 0.030 M., but the agreement with Lewis and Randall[25] is better for a greater

[24] loc. cit.
[25] loc. cit.

range namely, for concentrations from 0.005 M. to 0.050 M. From the data on the activity coefficients of hydrochloric acid it may be noted that there is a minimum of activity between 0.50 M. and 1.00 M. From this investigation we are led to the conclusion that the same type of variation is exhibited by the activity coefficients of hydrogen iodide, but that the minimum occurs at a lower concentration, 0.20 M. For the concentrations from 0.005 M. to 0.050 M. the assumption, that the activities of the halide ions are equal appears to be valid. Beyond that concentration the evidence is against the validity of the assumption. It would be desirable to have additional information from a similar study of hydrogen bromide solutions before passing a final opinion.

In regard to the slightly different values of activity coefficients from different sources, it is apparent that the difference lies mainly in the standard of reference chosen. Noyes and MacInnes [26] have arbitrarily set the activity coefficient at the lowest concentration at which the electromotive forces are dependable equal to the conductance viscosity ratio. In the case of hydrochloric acid the activity coefficient of 0.003324M. solution has been taken as .985. Lewis and Randall[27] have used as a basis of their values for hydrochloric acid a method of extrapolation described by Linhart.[28] Any error in either standard would influence the entire series of activity coefficients. Pearce and Hart[29] working with solutions of potassium bromide, and using a method similar to Noyes and MacInnes obtained activity coefficient products which agree with the results of those investigators in their work on potassium chloride solutions. In this research, using the method of Linhart[30], data have been obtained for hydrogen iodide which agree with his values of the activity coefficients of hydrogen chloride for a considerable range in the dilute solutions. Thus with the meager information at hand we are not justified in definitely stating which standard is correct.

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26 loc. cit.
27 loc. cit.
28 loc. cit.
29 loc. cit.
30 loc. cit.

SUMMARY

1. Measurement of the electromotive force of the cells:
H_2 | HI (c).....HI (c), AgI | Ag,
at various concentrations have been made.
2. The free energy decrease of the cell reaction, and the heat-content decrease of the cell reaction have been computed.
3. The free energy decrease accompanying the transfer of one mole of hydrogen iodide from the various concentrations to 0.10 molal have been calculated.
4. From the values of the electromotive force of the combination:
H_2|HI(.005)....HI(.005), AgI | AgAg | AgI, HI(c)....HI(c)|H_2
the activity coefficients have been calculated by the usual formula. From these values the activity coefficients at round concentrations have been determined. From the data obtained it has been concluded that the activities of the chloride and iodide ions are equal up to a concentration 0.05 molal but beyond that concentration the assumption does not appear to hold.

BIOGRAPHY

Arthur Roy Fortsch received his early education in the rural schools of Fayette County and Bremer County, Iowa. After two years of teaching in the rural schools, he entered Iowa State Teachers College, Cedar Falls, Iowa in 1911, receiving his A. B. degree in 1915. In 1915 he entered the University of Iowa. He received the degree of Master of Science in 1916. With the exception of thirteen months in the Army and a year teaching physics and chemistry in Mason City Junior College, Mason City, Iowa, he has continued in graduate work at the University since that time. He is a member of the American Chemical Society, Sigma Xi, Delta Sigma Rho, and and Gamma Alpha graduate scientific fraternity. At present he is employed as research chemist by the Standard Oil Company, Whiting, Indiana.